KINETICS OF STYRENE POLYMERIZATION AS DETERMINED WITH OPTICALLY ACTIVE MONOMERS

BY

CHARLES GILBERT OVERBERGER

B. S., Pennsylvania State College, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS. 1944

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Introduction

Although scores of "vinyl type" monomers have been polymerized alone and with other monomers and these products studied in detail, the actual mechanism of vinyl-type or addition polymerization is still the subject of much investigation and speculation. In order to pierce the darkness surrounding the mechanism of polymerization, numerous investigators have employed kinetic studies. Various analytical procedures have been used to follow the rate of a polymerization reaction. Isolation of the polymer, titration of the monomer by bromine, and change in volume have all been used for this purpose. Recently the change in optical rotation[1,2,3,4] during the polymerization of an optically active monomer has been used to obtain kinetic data.

In this thesis, the preparation of an optically active styrene derivative and a study of its polymerization was undertaken in order to clarify this problem.

Discussion

An optically active styrene derivative (*p*-vinylbenzyl-*d-sec.*-butyl ether) was synthesized in the following manner. *p*-Bromobenzyl bromide was treated with sodium *d-sec.*-butoxide. The resulting *p*-bromobenzyl-*d-sec.*-butyl ether upon treatment with cuprous cyanide produced the *p*-cyanobenzyl-*d-sec.*-butyl ether. The latter compound on treatment with methylmagnesium iodide produced the corresponding *p*-acetobenzyl-*d-sec.*-butyl ether which upon reduction with aluminum isopropoxide gave the corresponding carbinol, α-(*p*-benzyl-*d-sec.*-butyl ether) phenyl alcohol. The latter on dehydration with potassium hydrogen sulfate gave *p*-vinylbenzyl-*d-sec.*-butyl ether. Many of these reactions were first carried through with the methyl benzyl ether series so that there would be the least possible waste of optically active *sec.*-butyl alcohol.

Unfortunately, the change in rotation during polymerization of *p*-vinylbenzyl-*d-sec.*-butyl ether is not great and accurate kinetic studies were difficult to make. The indication is that the polymerization follows first order kinetics.

Another optically active styrene derivative whose synthesis was attempted was *p*-vinyl-*sec.*-butylbenzene. β-(*p*-*sec.*-Butylphenyl) ethyl alcohol was synthesized from pure *sec.*-butylbenzene by bromination to form the *p*-bromo derivative, subsequent formation of the Grignard of *p*-bromo-*sec.*-butylbenzene followed by reaction with ethylene oxide to give the desired product. Resolution of β-(*p*-*sec.*butylphenyl) ethyl alcohol by formation of the acid phthalate and subsequent formation of the brucine salt was not successful.

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Vita

The writer was born in Barnesboro, Pennsylvania, on October 12, 1920. He attended the public schools of this hamlet and was graduated from Barnesboro High School in 1937. He entered Pennsylvania State College in the Fall of 1937, where he was granted a B.S. Degree in June, 1941. He continued his studies in the graduate school of the University of Illinois from September, 1941, until the present time. Since February 1943, he has devoted all his research to the W. P. B. rubber program. During the past three years he has held the following appointments:

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